STABILITY AND DEMULSIFICATION OF THE WATER-IN-CRUDE EMULSIONS VIA CHEMICAL METHOD

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ABSTRACT

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Petroleum companies are familiar with the problems caused by the formation of water-in-crude oil emulsions, especially with those related to the increment of the crude oil apparent viscosity an their impact on the oil production. Many studies have been conducted to establish the existing relationship between the crude oil emulsions apparent viscosity and their water content. The emulsion stability results from the presence of interfacial barrier preventing coalescence of the dispersed water droplets. This is due to present of polar components such as asphaltenes, resins, wax and naphtenic acids in the crude oil. Therefore before transporting or refining the oil, it is essential to separate the water for economic and operational reasons. Minimizing the water level in the oil reduces pipeline corrosion and maximizes pipelines usage. Demulsification of crude oil forms an integral part of crude oil production and chemical demulsification is crucial step in demulsification sequence. In chemical demulsification, chemical known as demulsifier is added to the water-in-crude oil emulsion. The effect of chemical demulsification operations on the stability was assessed experimentally. In this regard, Amine group demulsifier were used. Using samples w/o, the data presented for several demulsifiers show a strong connection (correlation) between good performance (fast coalescence and the demulsifiers.

ABSTRAK

KESTABILAN DAN PENYAHEMULSI AIR DALAM EMULSI MINYAK MELALUI KAEDAH KIMIA

Syarikat-syarikat petroleum biasa dengan masalah-masalah disebabkan oleh pembentukan air dalam emulsi minyak mentah, terutama dengan mereka berkaitan dengan tambahan kelikatan ketara minyak mentah satu kesan mereka pada pengeluaran minyak. Banyak kajian telah dijalankan untuk menubuh perhubungan yang masih kekal antara kelikatan ketara emulsi minyak mentah itu dan kandungan air mereka. Keputusan-keputusan kestabilan emulsi daripada kehadiran sawar antara muka mencegah tautan titis-titis air tersebar. Ini merupakan disebabkan hadiah komponen-komponen kutub seperti asphaltenes, lilin dan naftenik asid-asid dalam minyak mentah. Lantarannya sebelum mengangkut atau menapis minyak, ia adalah penting untuk memisah air untuk alasan pengendalian dan ekonomi. Mengurangkan paras air dalam minyak mengurangkan kakisan saluran paip dan memaksimumkan penggunaan talian paip. Penyahemulsi borang-borang minyak mentah satu penting sebahagian daripada pengeluaran minyak mentah dan kimia penyahemulsi langkah genting dalam penyahemulsi urutan. Dalam kimia penyahemulsi, kimia dikenali sebagai penyahemulsian ditambah untuk air dalam emulsi minyak mentah. Kesan kimia penyahemulsi operasi pada kestabilan adalah ditaksir secara eksperimen. Dalam perhatian ini, kumpulan amina penyahemulsian telah digunakan. Menggunakan contoh-contoh w/o, data mempersembahkan untuk beberapa demulsifiers menunjukkan satu hubungan kuat (korelasi) antara prestasi baik (cepat tautan) dan demulsifiers.

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LIST OF ABBREVIATIONS

SARA	=	Saturates (including waxes), aromatics, resin and asphaltene
O/W	=	Oil-in-water emulsion
W/O	=	Water-in-oil emulsion
O/W/O	=	Oil-in-water-in-oil emulsion
W/O/W	=	Water-in-oil-in water emulsion

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Malaysia is important to the world energy markets because of its 75.0 trillion cubic feet of natural gas reserves and its net oil exports of over 260,000 barrels per day. Five oil fields (Guntong, Tabu, Palas, Semangkok and Irong Barat) of Esso Production Malaysian Incorporated (EPMI) contract areas in East Cost of Malaysia are having severe emulsion problems. Petronas oil fields of East Malaysia have also face the same problems. As a result, they have to some extent to sell their crude oil in the form of emulsion at low price due to the high cost for treating the emulsions (Hanapi *et. al*., 2006).

When crude oil is produced from an oil field well, it is generally accompanied with variable proportions of water. This water is emulsified by surface-active substances naturally present in the crude, which make the separation of water prior to crude commercialization difficult (Goldszal and Bourrel, 2000). The stability of the emulsion is ranging from a few minutes to years depending on the nature of the crude oil and to some extent the nature of water.

Crude oils consist of, in any case, a series of hydrocarbons such as alkanes, naphtenes, and aromatic compounds as well as phenols, carboxylic acids, and metals. A major fraction of sulfur and nitrogen compounds may be present as well. The carbon numbers of all these components range from 1(methane) through 50 or more (asphaltenes). Some of these components can form films at oil surfaces, and others are surface active. So, the tendency to form stable or unstable emulsions of different kinds varies greatly among different oil (Schramm, 1992).

In petroleum system, asphaltenes and resinous substances comprise a major portion of the interfacially active components of the oil. Asphaltenes and resins adsorb at the water-oil interfaces and form interfacial films that confer stability against phase separation (Sjoblom et al., 2003), (McLean et al., 1998) and (Strassner, 1968).

Understanding and controlling demulsification is of primary importance for breaking waste emulsions and for using emulsions in industrial processes that require emulsion destabilization as a main step. At drilling site, the recovered oil will contain some water and hydrophilic impurities which need to be removed before shipping and processing. The water concentration may vary, but a target specification for water and sediments removal may be 1% or less (Speight, 2007).

The breaking of emulsions (demulsification) is necessary in many applications such as environmental technology, painting, petroleum industry and waste-water treatments. Methods currently available for demulsification can be broadly classified as chemical, electrical and mechanical.

The treatment of water-in-crude oil emulsions involves the application of thermal, electrical and chemical process or their combinations. Thermal method or heat treatment in emulsion breaking is usually based on the overall economic picture of a treating facility. Temperatures are not high enough to significantly rise up water solubility in a particular crude oil, and high temperatures do not cause large amounts of asphaltenes to become insoluble in the crude oil and form an interface pad (Grace, 1992).

Electrical methods disturb the surface tension of each droplet, possibly by causing polar molecules to reorient themselves (Grace, 1992). This reorientation weakens the film around each droplet because the polar molecules are no longer intense at the droplets surface. This process does not typically resolve emulsions completely by itself, although it is an efficient and often required addition of chemicals or heat (Hanapi *et al*., 2006).

Chemical methods are the most common method of emulsion resolution in both oil field and refinery. The combination of heat and application of chemicals designed to neutralize the effects of emulsifying agents have great advantages of being able to break an interfacial film effectively; without the addition of new equipments or modifications of the existing equipment (Hanapi *et al*, 2006).

In order to devise optimum treatment for water-in-oil emulsions by using chemical treatment method, it is vital to understand how they are stabilized and destabilized the emulsion. Therefore, a comprehensive knowledge of crude oil emulsion stability and how the demulsifier destabilizes the crude oil emulsion is crucial, which need to be studied.

1.2 Problem Statement

The existence of water along with the crude oil that is being produced is undesirable because of problems directly correlated to foaming, corrosion of pipelines and tanks, higher power consumption, and increased volume and viscosity. When speaking of money, time and effort, some consider that the real problems where emulsions are recognized as a problem are in the petroleum industry.

In economical aspect, the separation of the crude oil emulsion necessary. The water presence is unwanted since it has high concentration of chloride salt, which causes some difficulties (i.e. refining difficulties) such as corrosion, coke deposition, foaming and poisoning of downstream catalyst and transportation difficulties such as pipeline and tank corrosion, scaling and fouling (Ariany, 2004). Extra power consumption and additional equipments are needed because the undesirable water occupies space in the processing equipment, thus it causes increasing of viscosity of the processing fluid, volume of involving equipments, expense pumping (Clark et. al. 1993; Li et. al., 1992; McMahon, 1992). Therefore, a premium is placed for treated oil and then, increasing API-degree through of water usually causes a higher price for the oil.

Water in oil emulsion occurs at many stages in the production and treatment of crude oil. About two third of petroleum production of every oil field exists in the form of water in oil emulsion. The emulsion stability results from the presence of interfacial barrier preventing coalescence of the dispersed water droplets. This is due to the present of polar components such as asphaltenes, resins, wax and naphtenic acids in the crude oil. Therefore, before transporting or refining the oil, it is essential to separate the water for economic and operational reasons. Minimizing the water level in the oil reduces pipeline corrosion and maximizes pipeline usage.

Macro emulsions are thermodynamically unstable, and given sufficient time, will separate out naturally. However due to the growing importance and demand for the petroleum oil worldwide, it is not feasible to wait for nature to do the job. In light of this, many techniques have been developed to do that kind of job, in the shortest period of time, and with least expenditure. The process of separation industrially is referred to as demulsification. The most widely used method of treating crude oil emulsions is chemical demulsification.

The oil industry frequently characterizes crude oils in relation to their geographical starting place. The main reason for this is that oils from particular geographical regions have distinctive properties, and they can be different in consistency from a semi solid to a light volatile fluid.

1.3 Objectives

The objective of this study is focus on crude oil emulsion stability using two different crude oil samples as well as an investigation on chemical demulsification is carried out for characterization and selecting the demulsifiers systematically.

1.4 Scope of Study

To achieve the objectives, scopes have been identified in this study. The scopes of this study are listed as below:

i. Characterization of emulsions (w/o) in terms of physical and chemical properties.
ii. Properties of stable (w/o) emulsions and investigate their stability parameters.
iii. Overall investigation of chemical demulsification method.
iv. Comparison between chemical method and heating method.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Crude oil is a complex fluid containing asphaltenes, resins and napthenic acid. Asphaltenes is the heaviest and most polar fraction in the crude oil and responsible in rising up the variety of nuisances and stabilized the water in oil emulsion that occurred during crude oil production. It is widely known that deposition and flocculation of asphaltenes may be occurred when the thermodynamic equilibrium is disturbed.

The water and oil phases are co-produced during oil production and transportation. The dispersion of water droplets in oil or oil droplets in water will be formed by sufficient mixing energy from the refinery. The interfacial active agents in the crude oil such as asphaltenes, resins and naphtenic acid may accumulate at the water-oil interface and hinder the droplets to separate. Among these components, asphaltenes are believed to be the major causes in stabilized the emulsion. This is because they tend to adsorb at water-in-crude oil interfaces to form a rigid film surrounding the water droplets and protect the interfacial film from rupturing during droplet-droplet collisions. Consequently, the formation of particularly stable water-in-crude oil emulsion is facilitated.

Emulsion problems in crude oil productions resulted in a demand for expensive emulsion separation equipment such as water treaters, separators and coalescers. Hence, chemical demulsification is the suitable method from both operational and economic point of view to break the crude oil emulsion. A chemical agent typically acts on the interfacial film by either reacting chemically with the polar crude oil components or by modifying the environment of the demulsification. Among chemical agents, interfacial-active demulsifiers, which weaken the stabilizing films to enhance droplets coalescence, are preferred due to lower additions rates needed (Abdurrahman *et al.*, 2007).

Emulsions of oil and water are one of many problems directly associated with the petroleum industry, in both oil-field production and refinery environments. Whether these emulsions are created inadvertently or are unavoidable, as in the oil field production area, or are deliberately induced, as in refinery desalting operations, the economic necessity to eliminate emulsions or maximize oil-water separation is present. Furthermore, the economics of oil-water separation dictate the labor, resources and monies dedicated to this issue. Before we describe the methods and economics of emulsion breaking at commercial facilities, we will restate several key concepts concerning emulsions and petroleum industry (Fingas & Fieldhouse, 2004).

Therefore, considering many aspects that are related in petroleum processing, it is important to develop the demulsifier formulation to solve the emulsion problems. The aspects that are important to be studied are such as crude oil composition and characterization, emulsions and emulsion stability, stabilization of water-in-crude oil emulsions and destabilization of crude oil emulsions. The thesis statement for this study is the water-in-crude oil emulsion can be separate using chemical and have different properties for different geographical region.

2.2 Crude Oil Emulsion Composition

2.2.1 Introduction

Crude oil contains complex mixture of organic composite. Its composition can vary due to its reservoir's place of origin, depth and age (Speight, 2007). Crude oils mainly consists the mixture of hydrogen and carbons, with little amount of sulphur, nitrogen and oxygen as well as structures with incorporated metallic molecules such as nickel, vanadium, copper and iron (Speight, 2007). There is a broad variation in physical properties from the lighter oils to the bitumens.

Crude oils consist of light hydrocarbon such as gasoline, asphaltenes, resins, waxes and napthenic acid. The asphaltene content of petroleum is an important aspect of fluid process ability. The method of dividing crude oil into four major fractions: saturates (including waxes), aromatics, resins and asphaltenes is called SARA fractionation, based on their polarity and solubility in the solvent. The method of dividing crude oil into these four fractions is illustrated in Figure 2.1.

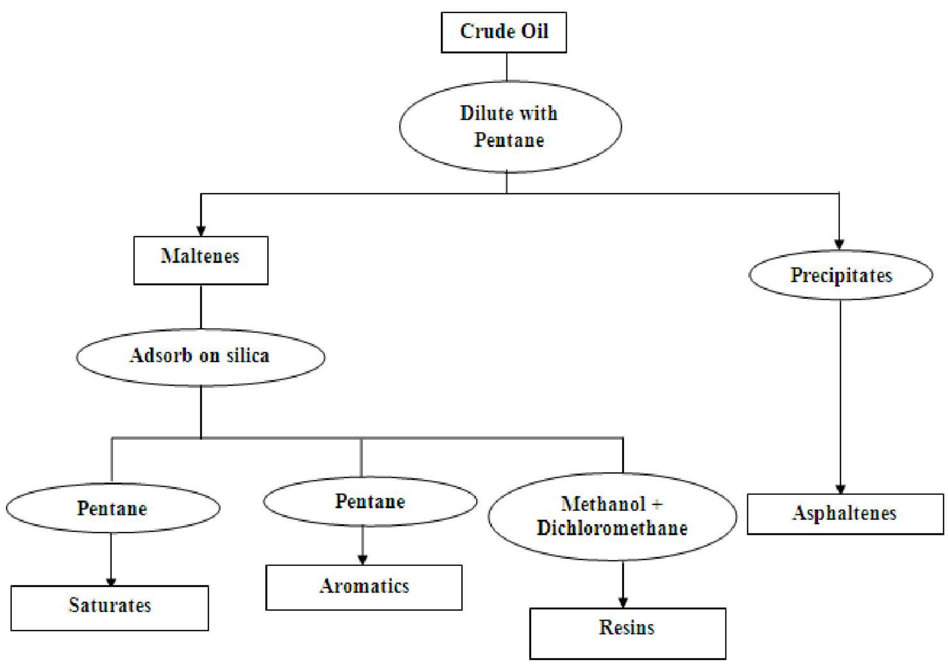

Figure 2.1: Schematic of SARA fractionation of crude oils

The fractions of crude oil that have been identified as contributing to the formation of water-in-oil emulsion includes asphaltenes, resins and waxes and can exist in both the dissolved and particulate forms.

2.2.2 Emulsion Stability Parameter

Viscosity is the measure of the flow properties of the oil/material (Cormack, 1999). Low viscosity implies a mobile liquid and high viscosity denotes the materials that are resistant to flow, such as heavy fuel oils (Cormack, 1999). Most of the crude oils and refined products have viscosities from approximately 5 to 25000 centistokes at 15°C (Nordvik et al., 1996). Viscosity of an emulsion is governed by the factors stated below (Johnsen and Ronningsen, 2003).

i. Viscosity of the continuous phase
ii. Viscosity of the dispersed phase
iii. Volume fraction of the dispersed phase
iv. Temperature
v. Average droplet size and size distribution
vi. Presence of solids in addition to the dispersed phase liquid
vii. Shear rate
viii. Nature and concentration of the emulsifying agent

The effect of increased temperature is the sum of changes in several parameters. For instance, changes in the solubility of the crude oil surfactants or injected treating chemicals may occur as a result of increasing temperature. The density of the oil is reduced faster than the density of water as temperature increases, thereby accelerating the settling.

Bulk viscosity of the crude oil decreases with the increasing temperature, hence facilitating an increased collision frequency between water droplets; in addition to increasing the settling rate. Essential for the coalescence, especially in flocculated systems, is the influence of the interfacial viscosity. Depending on the type of interface the interfacial viscosity may decrease, increase or remain unchanged with increased temperature (Jones *et. al*., 1978).

With highly paraffinic crudes found in the North Sea, waxes are strongly correlated to the stability of emulsions. The wax may contribute to the stability through particle stabilisation, or from increasing the viscosity of the crude oil. Therefore, melting and crystallisation sequence of wax is of importance for the stabilising properties of these compounds (Graham *et. al*., 1983). High operational temperatures may however result in high losses of light end molecules, and consequently an increased potential for asphaltene deposition.

As the crude oil weathers, its viscosity increases due to the progressive loss of the light volatile (lower molecular weight) fractions .Viscosity increases with decrease in temperature (Cormack, 1999). Evaporation and emulsification increases the viscosity of the fresh spilled oil (Cormack, 1999).

Other factors that usually favour emulsion stability is low interfacial tension, high viscosity of the bulk phase and relatively small volumes of dispersed phase. A narrow droplet distribution of droplets with small sizes is also advantageous, since polydisperse dispersions will result in a growth of large droplets on the expense of smaller ones; an effect termed Ostwald ripening (Sjöblom, 1996).

2.3 Crude Oil Emulsion Formations and Stability

2.3.1 Introduction

Usually, no emulsions are formed within the petroleum layer. Emulsion formation begins during the movement of petroleum to the mouth of the oil well and intensifies during further transport of petroleum in pipes (i.e. emulsions are predominant where there is the potential for continuous mixing of petroleum and water). The intensity of emulsion formation in an oil well depends on the method of petroleum extraction. Then, in turn, is defined by the character of the oil wells, time of its operation and physical-chemical properties of the petroleum.

When petroleum is extracted from oil wells using the natural layer pressure (which is typical in the initial period of oil well operation), there is usually a very high rate of extraction of the oil from the oil well. The intensity of petroleum mixing with water in elevating pipes of the oil increases due to dispersion of the solved gases at decreasing pressure. This leads to emulsion formation at the early stages of movement of the petroleum-water mixture.

During deep pumping extraction of petroleum, emulsion formation occurs in the valves, in the pump cylinders and in the elevating pipes during the reciprocating movement of pump bars.

2.3.2 Classification of emulsions

Emulsion has long been of great practical interest due to their widespread occurrence in everyday life. They may be found in important areas such as food, cosmetics, pulp and paper, pharmaceutical and agricultural industry. Petroleum emulsions may not be as familiar but have a similar long-standing, widespread, and important occurrence in industry, where they are typically undesirable and can result in high pumping costs, pipeline corrosions, reduced throughput and special handling equipment. Emulsions may be encountered at all stages in the petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions.

An emulsion is usually defined as a system in which one liquid is relatively distributed or dispersed, in the form of droplets, in another substantially immiscible liquid. The emulsion formation is a result of the co-production of water from the oil reservoir. During processing, pressure gradients over chokes and valves introduce sufficiently high mechanical energy input (shear forces) to disperse water as droplets in the oil phase.

In the petroleum industry the usual emulsions encountered are water droplets dispersed in the oil phase and termed as water-in-oil emulsion (W/O), conversely, if the oil is the dispersed phase, it is termed oil-in-water (O/W) emulsion.

Two types of emulsion are readily distinguished in principle, depending upon which kind of liquid forms the continuous phase (Figure 2.2):

i. Oil-in-water (O/W) for oil droplets dispersed in water
ii. Water-in-oil (W/O) for water droplets dispersed in oil.